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AMBIENT GASEOUS FLUORIDE MEASUREMENTS IN THE TENNESSEE VALLEY: 1970-1979

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AIR RESOURCES PROGRAM

TVA/ONR/ARP-81-3

TENNESSEE VALLEY AUTHORITY

Office of Natural Resources

Air Resources Program

AMBIENT GASEOUS FLUORIDE MEASUREMENTS IN THE TENNESSEE VALLEY: 1970-1979

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March 1981

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AMBIENT GASEOUS FLUORIDE MEASUREMENTS IN THE TENNESSEE VALLEY: 1970-1979

EXECUTIVE SUMMARY

This report summarizes the results of monthly gaseous fluoride (GF) monitoring in the vicinity of TVA's National Fertilizer Development Center (NFDC), Johnsonville Steam Plant, Shawnee Steam Plant, and the five regional air quality trend stations. Although there is no national ambient air quality standard for GF, several states, including Tennessee and Kentucky, have adopted ambient GF standards.

The TVA use of the limed-filter GF monitoring method predated the development of the Tennessee and Kentucky GF standards which utilize more rigorous monitoring methods. The TVA data, therefore, are not comparable to either of these state standards. The TVA data are, however, directly comparable to the Maryland state standard which is based upon the annual average of monthly limed-filter measurements. The Maryland standard is used as a comparison benchmark.

The major conclusions and recommendations are as follows:

- At NFDC, GF levels have generally declined with the gradual elimination or control of fluoride emitting facilities. Although the Maryland standard was exceeded on three occasions during the early 1970's, the most recent data reflect values less than one-half the Maryland standard. TVA GF monitoring is no longer necessary at NFDC and should only be reconsidered if a new TVA fluoride emissions source is sited in the area.

- Consistently high levels of GF in the vicinity of Johnsonville Steam Plant are the result of emissions from the Consolidated Aluminum Corporation (CONALCO) smelting facility. Violations of the Maryland standard have been commonplace and, at one station, GF levels have been 5 to 15 times the Maryland standard. These GF levels constitute a serious threat to local vegetation and grazing animals. Although it is apparent that the Johnsonville Steam Plant is not responsible for these exceptional GF levels, it is recommended that TVA GF monitoring be continued at the most heavily impacted station until GF levels are reduced to a safe, stable level below the Maryland standard.

- GF levels in the vicinity of Shawnee Steam Plant have remained stable at less than one-half the Maryland standard. The principal sources of fluoride emissions in this area are the Paducah (Kentucky) Gaseous Diffusion Plant and the Allied Chemical Company (in Metropolis, Illinois). TVA GF monitoring is no longer necessary in this area and should only be reconsidered if a new TVA fluoride emissions source is sited there.

- GF levels at the five regional trend stations have shown a two-to-three-fold increase during the 1970's. Even though GF levels remain less than one-third the Maryland standard, this trend may reflect an overall regional increase. It is recommended that GF monitoring (which was discontinued in May 1979) be reinstated at the regional trend stations to continue tracking the long-term changes in regional GF levels.

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AMBIENT GASEOUS FLUORIDE MEASUREMENTS IN THE TENNESSEE VALLEY

INTRODUCTION

OBJECTIVE

This report summarizes the results of monthly gaseous fluoride (GF) monitoring (limed-filter method) at three Tennessee Valley Authority (TVA) source-specific monitoring networks and at five regional air quality trend stations from 1970 through 1979. Descriptive figures are presented, temporal behavior discussed, comparisons to standards made, and recommendations given for future TVA fluoride monitoring strategies.

BACKGROUND

The damaging effects of fluoride emissions on vegetation have been recognized since the late 19th century.[1] Ambient gaseous fluorides (primarily hydrogen fluoride [HF]) are very phytotoxic air pollutants and cause vegetation damage at very low concentrations.[2] Fluoride contamination of forage crops, by accumulation of both gaseous and particulate fluoride, can also lead to pathological fluorosis in grazing animals.[3] Ambient fluoride levels, however, do not appear to pose a significant threat to human health.[4] As is true with most air pollutants, much is known about the acute effects of fluorides (high concentration, short exposure), but relatively little about their chronic effects (low concentration, long exposure).

Since World War II, the expansion of old and development of new fluoride-emitting industrial sources have led to an increasing concern about the effects of fluoride. Major manmade sources of fluoride emissions include

aluminum, phosphate fertilizer, uranium, iron smelting, and ceramics industries.[5] Fluoride emissions from these sources are sometimes capable of producing high ground-level concentrations resulting in acute vegetative injury. Coal combustion, too, is a substantial source of atmospheric fluoride even though fluorine is only considered as a trace element in most coals. Fluoride emissions from coal combustion sources are not considered sufficient to result in acute ground-level damage, but certainly should be considered as a major source in terms of chronic exposure.

There are no national ambient air quality standards for GF although ambient standards and guidelines have been adopted by some states. Of the states in the TVA power service region, only Tennessee and Kentucky have GF standards. However, because TVA's GF sampling program predated these state standards, TVA's limed-filter monitoring method is not comparable to the state-prescribed methods. Therefore, the Maryland GF standard (2.0 micrograms of fluoride per hundred square centimeters per day [μgF/100 cm^2/day)] which is based on the annual average of monthly limed-filter samples, will be used as a point of reference for TVA measurements.

MATERIALS AND METHODS

SAMPLING AND CHEMICAL ANALYSIS

The limed-filter method for quantitative determination of gaseous atmospheric fluoride has been in use for several decades.[6] This method is based on the observation that GF will react with lime (CaO) to form calcium fluoride (CaF_2). The method has proven to be highly reliable and cost effective in: (1) delineating areas with GF pollution and determinating the relative impact within those areas, and (2) reflecting long-term changes in ambient GF concentrations. This method does not measure particulate fluorides which may comprise a substantial portion of total atmospheric fluorides.

The limed filters were prepared by dipping Whatman No. 2 filters in a lime slurry and drying them in a forced-air oven at 100°C. Prepared filters were stored in sealed containers before and after field exposure. In the field, filters were exposed in an open air shelter for 28 to 32 days and returned to the TVA analytical laboratory for analysis. In the laboratory, filters were diced, placed in plastic beakers, diluted with a total ionic strength adjustment buffer (TISAB), and stirred. The fluoride content was determined with fluoride specific ion electrodes. These concentrations were then converted to and reported as micrograms of fluoride per hundred square centimeters per day ($\mu gF/100\ cm^2/day$).[7]

DATA ANALYSIS

The monthly fluoride data were reported to the Air Resources Program for validation and data analysis. Data used in this report were validated and analyzed with the Statistical Analysis System (SAS) on TVA's main computer system.[8] All graphics displays were created with the Tektronics 4081 Computer Graphics System.

RESULTS AND DISCUSSION

GASEOUS FLUORIDES IN THE VICINITY OF NFDC

At its peak, the limed-paper fluoride monitoring network at NFDC consisted of nine stations (figure 1). The first of these stations was installed in December 1963 and the last in November 1974. The last operating station, monitor 10, was discontinued in August 1980. GF monitoring data collected prior to 1970 were not stored in a computer-accessible file, and have not been considered in this analysis.

The principal sources of GF emissions at NFDC were the phosphorus, phosphoric acid, and phosphate fertilizer production facilities. With the shutdown of the phosphorus and phosphoric acid facilities in May of 1976, NFDC fluoride emissions were greatly reduced. Non-TVA fluoride sources in the Muscle Shoals, Alabama, area included aluminum reduction, ceramics, and phosphate fertilizer industries.

In figure 2, the plot of GF levels over time for those five NFDC monitoring stations (with the longest period of record during the 1970's) revealed, overall, a slight decline over the decade. However, the response was not homogeneous for all stations. Stations 2 and 3, northwest of NFDC, recorded the highest annual average GF concentrations, 2.22 and 2.11 $\mu F/100\ cm^2/day$, respectively. The Maryland standard was exceeded three times during the early 1970's although the most recent data (station 10) reflected annual averages less than one-half the standard.

GASEOUS FLUORIDES IN THE VICINITY OF THE TVA JOHNSONVILLE STEAM PLANT

The limed-paper fluoride monitoring network at the Johnsonville Steam Plant consisted of six stations (figure 3). The first of these stations

was installed in October 1969 and the last in June 1970. These stations were sited to quantify and determine the spatial distribution of ambient GF pollution in the vicinity of the CONALCO aluminum reduction plant. Only station 8 is still in operation. The other stations were discontinued in April 1978.

The principal source of fluoride emissions in the Johnsonville area is the CONALCO plant. It is the only uncontrolled primary aluminum reduction plant in the United States. While it must be acknowledged that the TVA plant does contribute (0.6 tons F per day) to the GF levels in the Johnsonville area, the source strength of the aluminum reduction plant (8.7 tons F per day) is a far more significant factor in determining excessive ground-level concentrations.

For the ten years of data collected at this network (1970-1979), the overall trend of monthly fluoride levels has remained unchanged (figure 4). With the exception of station 7 which served as a control station, all of the stations have, at some time, exceeded the Maryland standard. GF levels at station 8, an order of magnitude greater than those at the other stations, have had annual averages ranging from 10.9 to 29.0 μgF/100 cm^2/day, 5 to 15 times the Maryland standard.

GASEOUS FLUORIDES IN THE VICINITY OF THE TVA SHAWNEE STEAM PLANT

The limed-paper fluoride monitoring network at the Shawnee Steam Plant consisted of two stations (figure 5). They were both installed in November 1971 and removed in March 1978. These monitors were sited to determine if fluoride emissions from uranium enrichment process were contributing to the air pollution injury to soybeans.

The principal sources of fluoride emissions in the Shawnee area are the Paducah (Kentucky) Gaseous Diffusion Plant and the Allied Chemical Company (in Metropolis, Illinois). As with the Johnsonville plant, the Shawnee plant contributes to the atmospheric burden of fluorides, but, relatively, is not a strong source.

For the approximately six years of data collected at this network (1972-1978), the overall trend of GF levels remained unchanged (figure 6). The two highest annual values, both less than one-half the Maryland standard, occurred in 1974 with values of 0.93 and 0.82 µgF/100 cm^2/day at stations 6 and 7, respectively.

GASEOUS FLUORIDES IN THE VICINITY OF THE TVA REGIONAL AIR QUALITY TREND STATIONS

Limed-filter fluoride monitoring at the five regional trend stations began at the Hytop station in December 1969 and at the other stations in April and May 1971 (figure 7). All fluoride monitoring at these stations was discontinued in May 1979. There are no known manmade sources of GF in the immediate vicinity of any of the regional trend stations. These monitors were installed to establish a baseline record of ambient GF concentrations.

For the ten years of data collected, the overall trend has been decidedly upward (figure 8) with the annual maximum values for each station (ranging from 0.45 to 0.69 µgF/100 cm^2/day) occurring in 1977 and 1978. While the annual means for these stations remain well below the Maryland standard, an apparent twofold to threefold increase is striking and may be indicative of a long-term change in regional fluoride levels.

CONCLUSIONS AND RECOMMENDATIONS

NATIONAL FERTILIZER DEVELOPMENT CENTER

Conclusion: GF levels in the vicinity of NFDC declined slightly during the 1970's. The most recent values were approximately one-half the Maryland standard.

Recommendation: GF monitoring is not necessary at NFDC and should only be reconsidered if a new TVA fluoride emissions source is sited in the area.

JOHNSONVILLE STEAM PLANT

Conclusion: GF levels in the vicinity of the Johnsonville Steam Plant have frequently exceeded the Maryland standard. These elevated ambient fluoride levels, principally due to fluoride emissions from the CONALCO aluminum reduction plant, constitute an obvious threat to local vegetation and grazing animals.

Recommendation: GF monitoring should be continued at station 8 until such time that ambient fluoride levels can be reduced to a safe, stable level below the Maryland standard. Since vegetation damage from acute exposure to gaseous fluorides may mistakenly be attributed to the sulfur dioxide emissions from the Johnsonville Steam Plant, TVA may consider converting station 8 to a continuous (one-day or one-hour samples) monitoring method for improved temporal resolution. In addition, the limed-filter monitoring method should be retained to provide information on the long-term trends.

SHAWNEE STEAM PLANT

Conclusion: GF concentrations in the vicinity of Shawnee Steam Plant remained relatively stable at levels one-half the Maryland standard.

Recommendation: GF monitoring is not necessary at Shawnee Steam Plant and should only be reconsidered if a new TVA fluoride emissions source is sited in the area.

REGIONAL TREND STATIONS

Conclusion: Annual GF levels at the five regional trend stations were one-quarter to one-half the Maryland standard. However, the levels at each station also indicated a pronounced twofold to threefold increase over the years.

Recommendation: Limed-paper GF monitoring (which was discontinued in May 1979) should be reinstated at the trend stations for a minimum of two years to determine whether or not regional fluoride levels have continued to increase. At the end of two years these data will be examined to determine whether or not further monitoring is warranted.

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REFERENCES

1. Weinstein, L. H. "Fluoride and plant life," Journal of Occupational Medicine, 19:1 pp. 49-77 (January 1977).
2. Jacobson, J. S. and A. C. Hill, Editors. Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1970. pp. D1-D6.
3. Isreal, G. W., "A field study of the correlation of static lime paper samples with forage and cattle urine," Atmospheric Environment, Vol. 8, pp. 167-181 (1974).
4. Smith, F. A., and H. C. Hodge, "Airborne fluorides and man: part II," CRC Critical Reviews in Environmental Control, pp. 1-25 (February 1979).
5. Thompson, R. J., T. B. McMullen, and G. B. Morgan, "Fluoride concentrations in the ambient air," Journal of the Air Pollution Control Association, Vol. 21, pp. 484-487 (1971).
6. Adams, D. F., "A quantitative study of the limed filter paper technique for fluorine air pollution studies," International Journal of Air and Water Pollution, 4:3,4 pp. 247-255 (1961).
7. Israel, G. W., "Evaluation and comparison of three atmospheric fluoride monitors under field conditions," Atmospheric Environment, Vol. 8, pp. 159-166 (1974).
8. Helwig, J. T. and K. A. Council, Editors. SAS User's Guide, 1979 Edition, SAS Institute, Inc. Raleigh, North Carolina, (1979).

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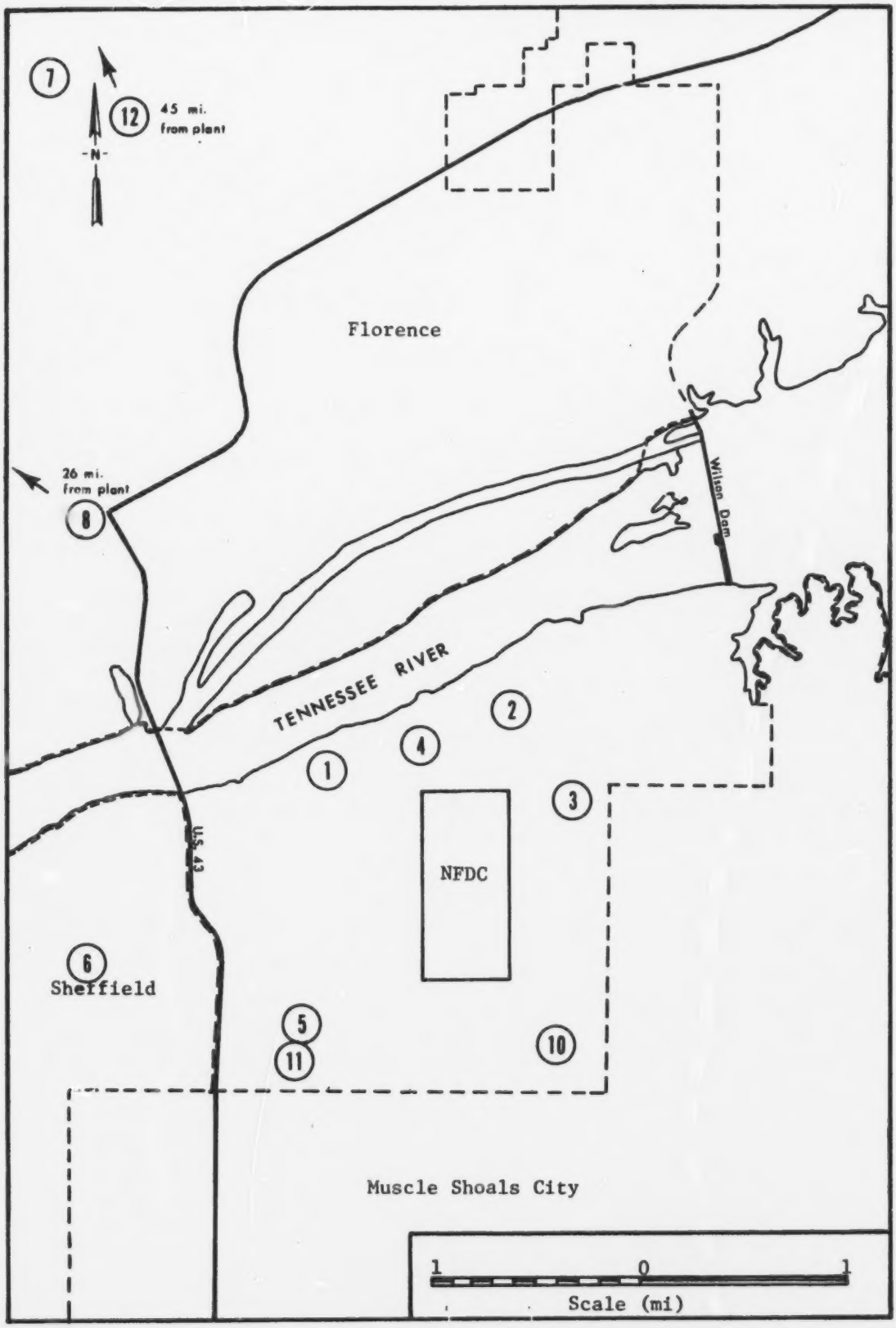
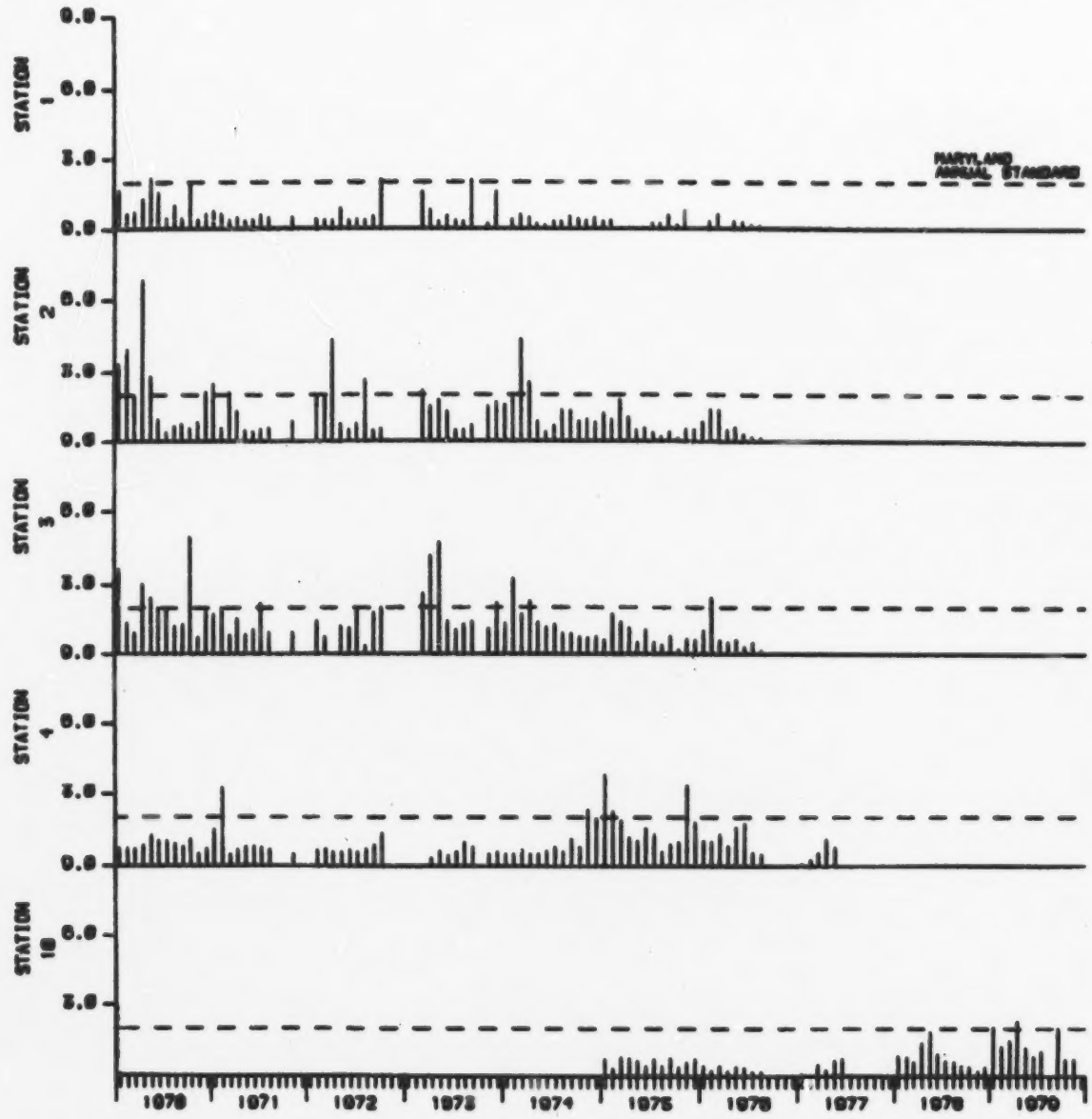


Figure 1. GASEOUS FLUORIDE MONITORING NETWORK AT THE NATIONAL FERTILIZER DEVELOPMENT CENTER

FIGURE 2 MONTHLY FLUORIDATION RATES AT THE NATIONAL FERTILIZER DEVELOPMENT CENTER (1970-1979) (ug F/100 sq cm/day)



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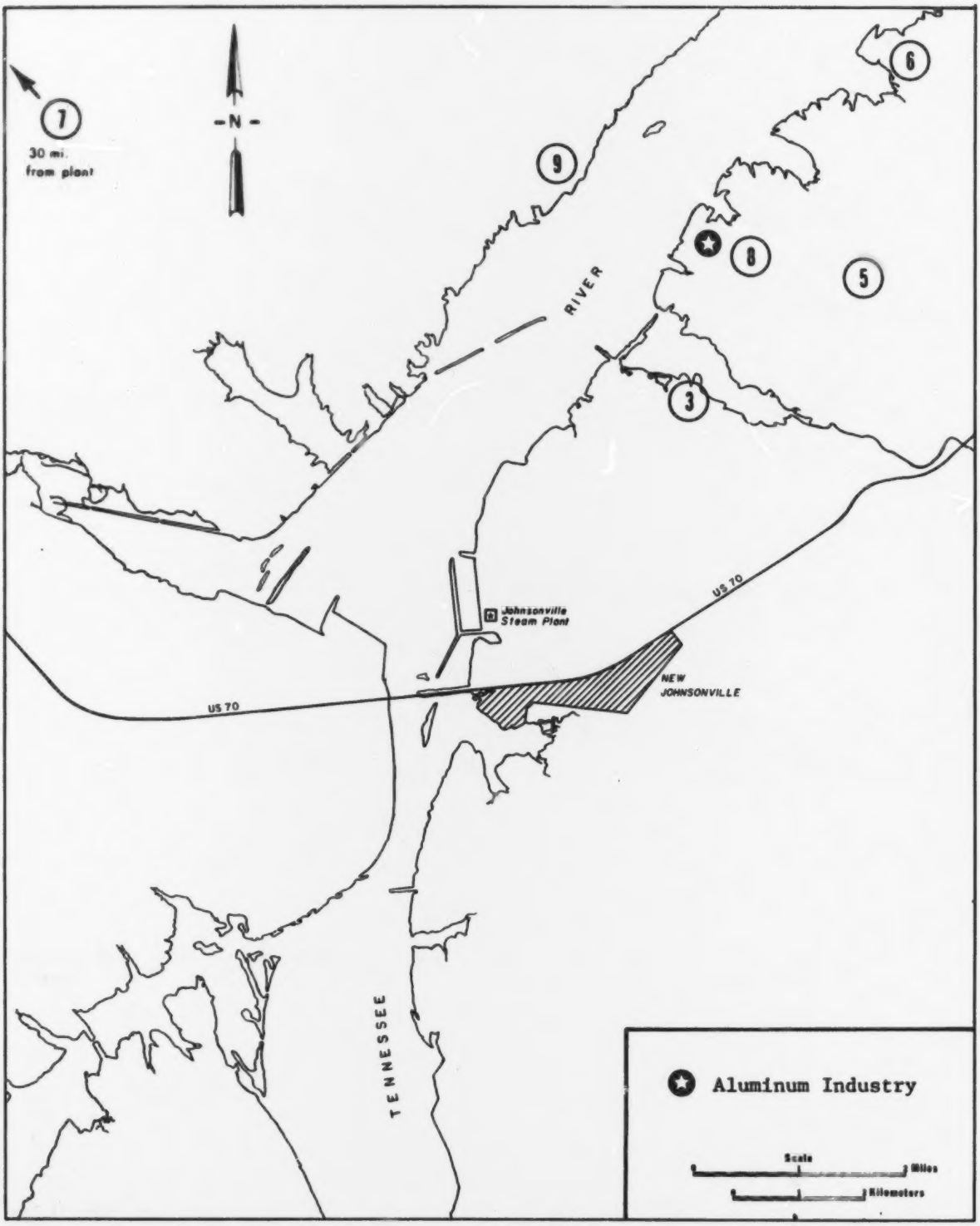

Figure 3. GASEOUS FLUORIDE MONITORING NETWORK AT THE JOHNSONVILLE STEAM PLANT

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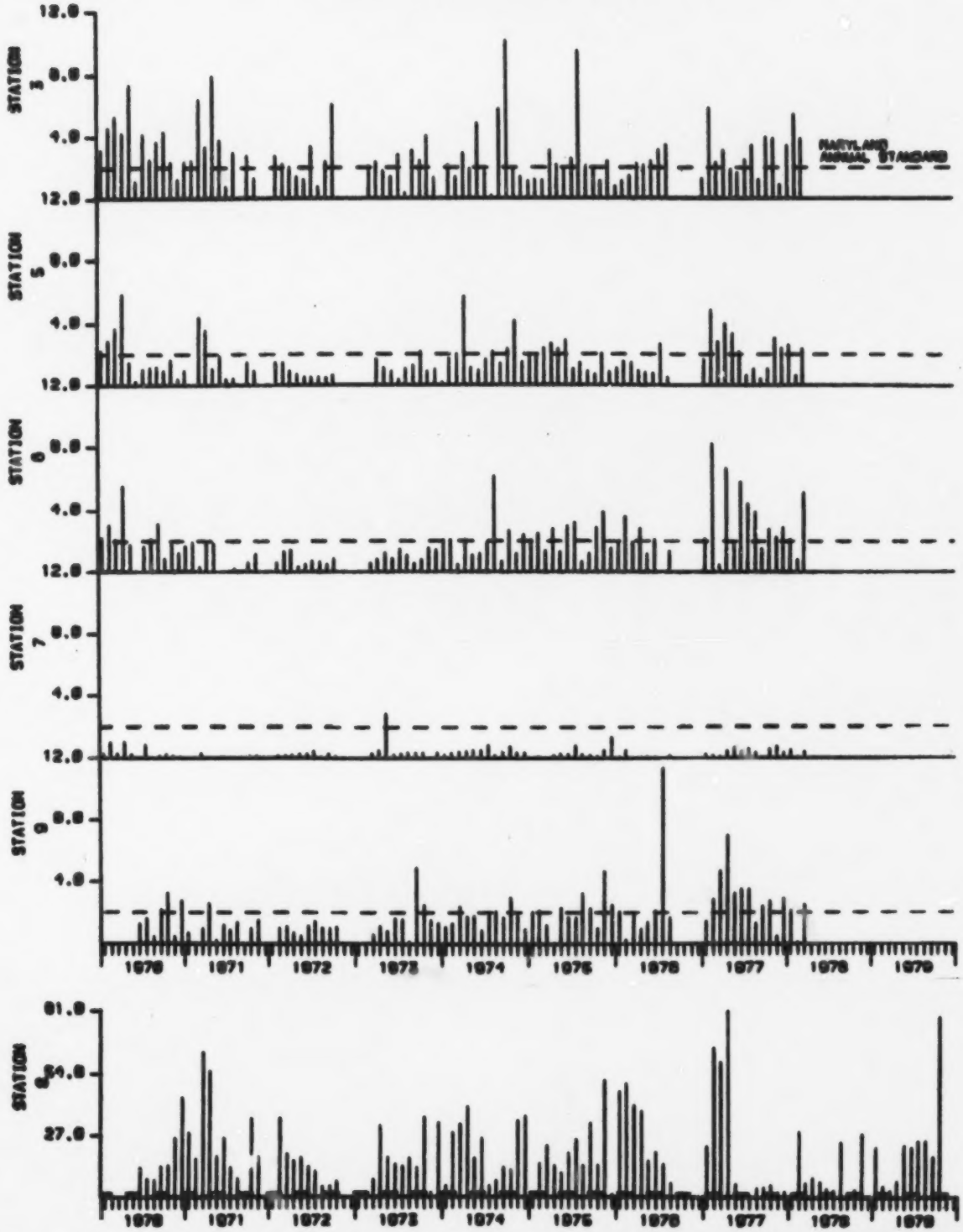
FIGURE 4 MONTHLY FLUORIDATION RATES AT THE TVA JOHNSONVILLE STEAM PLANT (1970-1979)
(ug F/100 sq cm/day)



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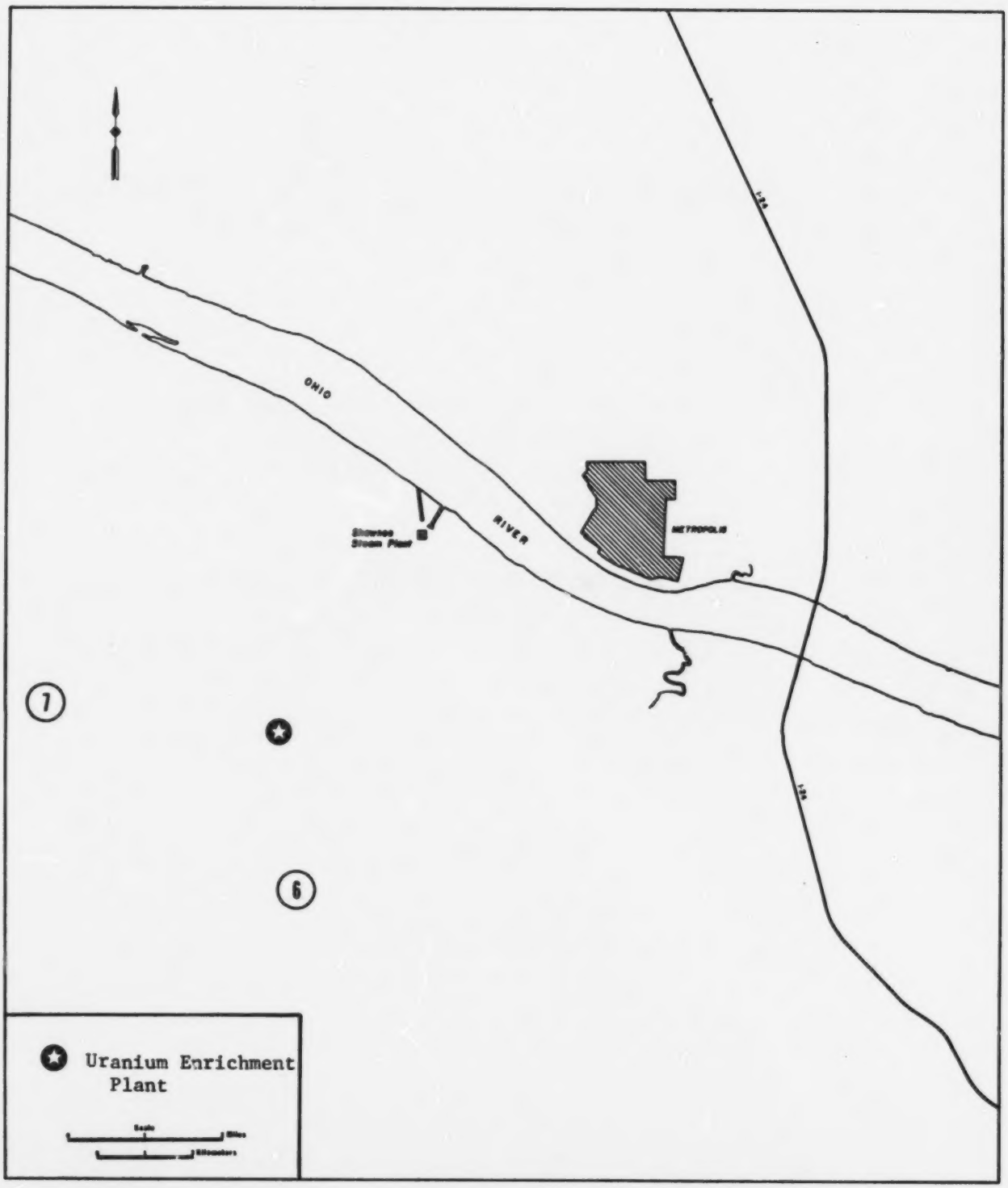

Figure 5. GASEOUS FLUORIDE MONITORING NETWORK AT THE SHAWNEE STEAM PLANT

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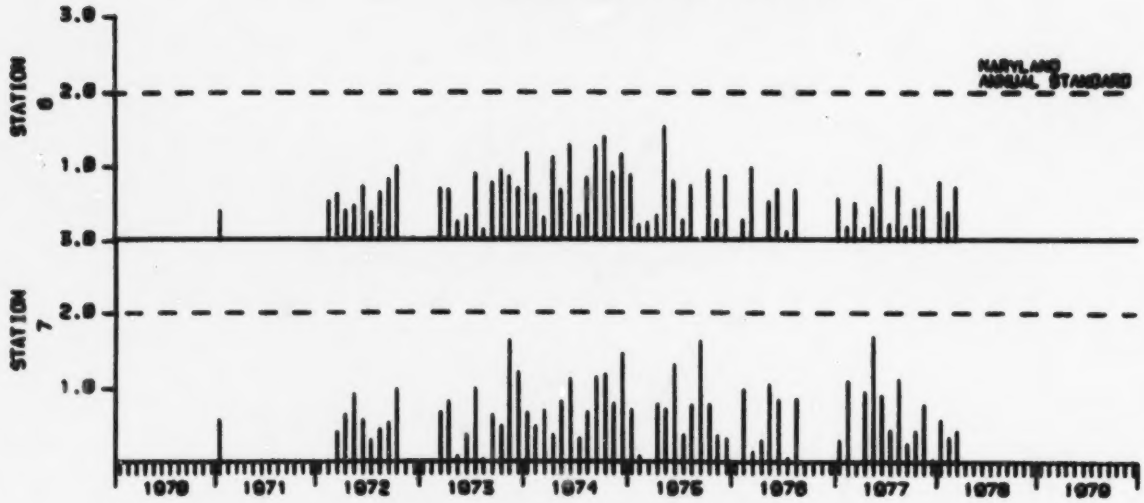
FIGURE 8 MONTHLY FLUORIDATION RATES AT THE TVA SHAWNEE STEAM PLANT (1970-1979) (ug F/100 sq cm/day)



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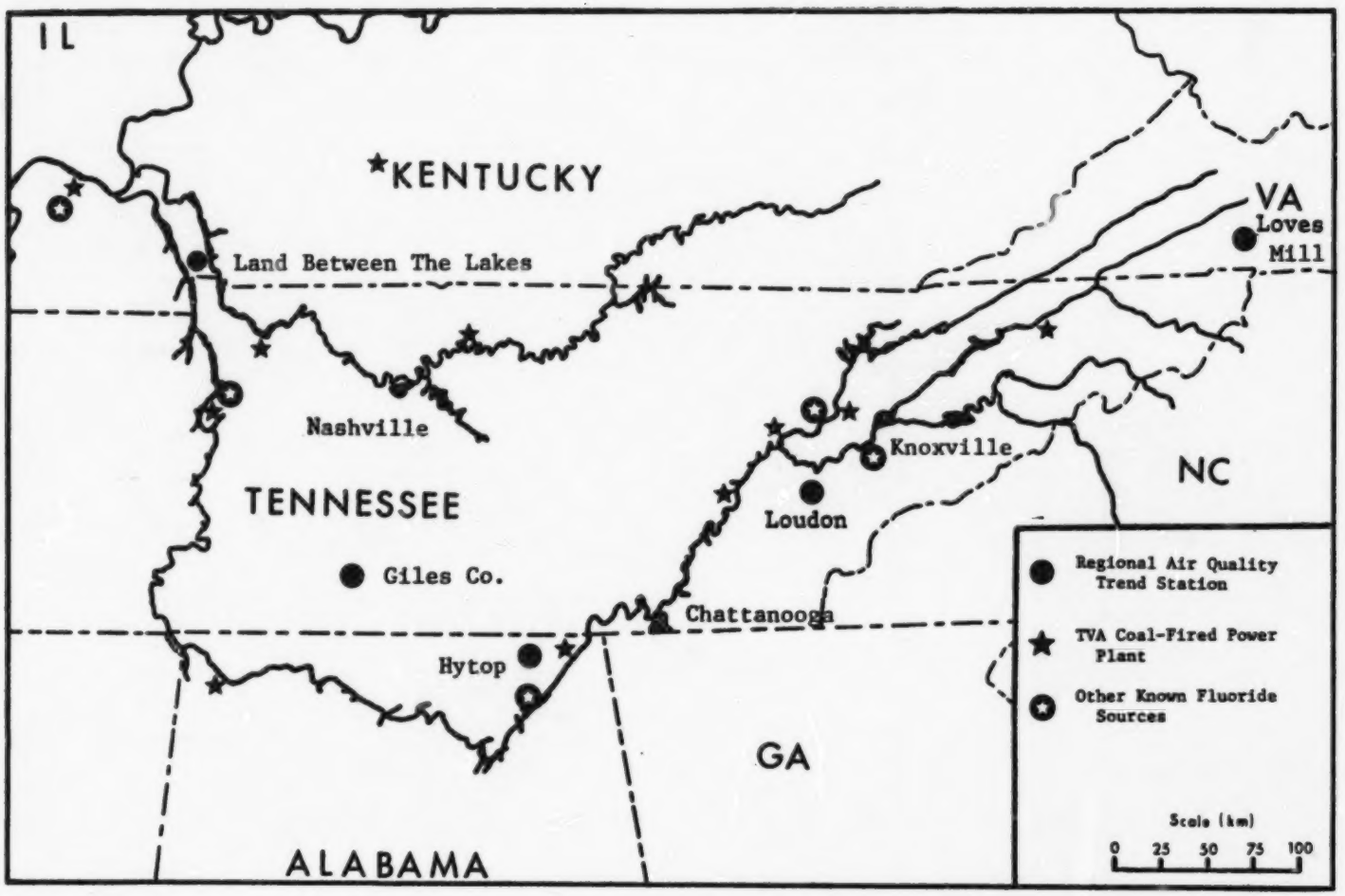

Figure 7. REGIONAL AIR QUALITY TREND STATIONS

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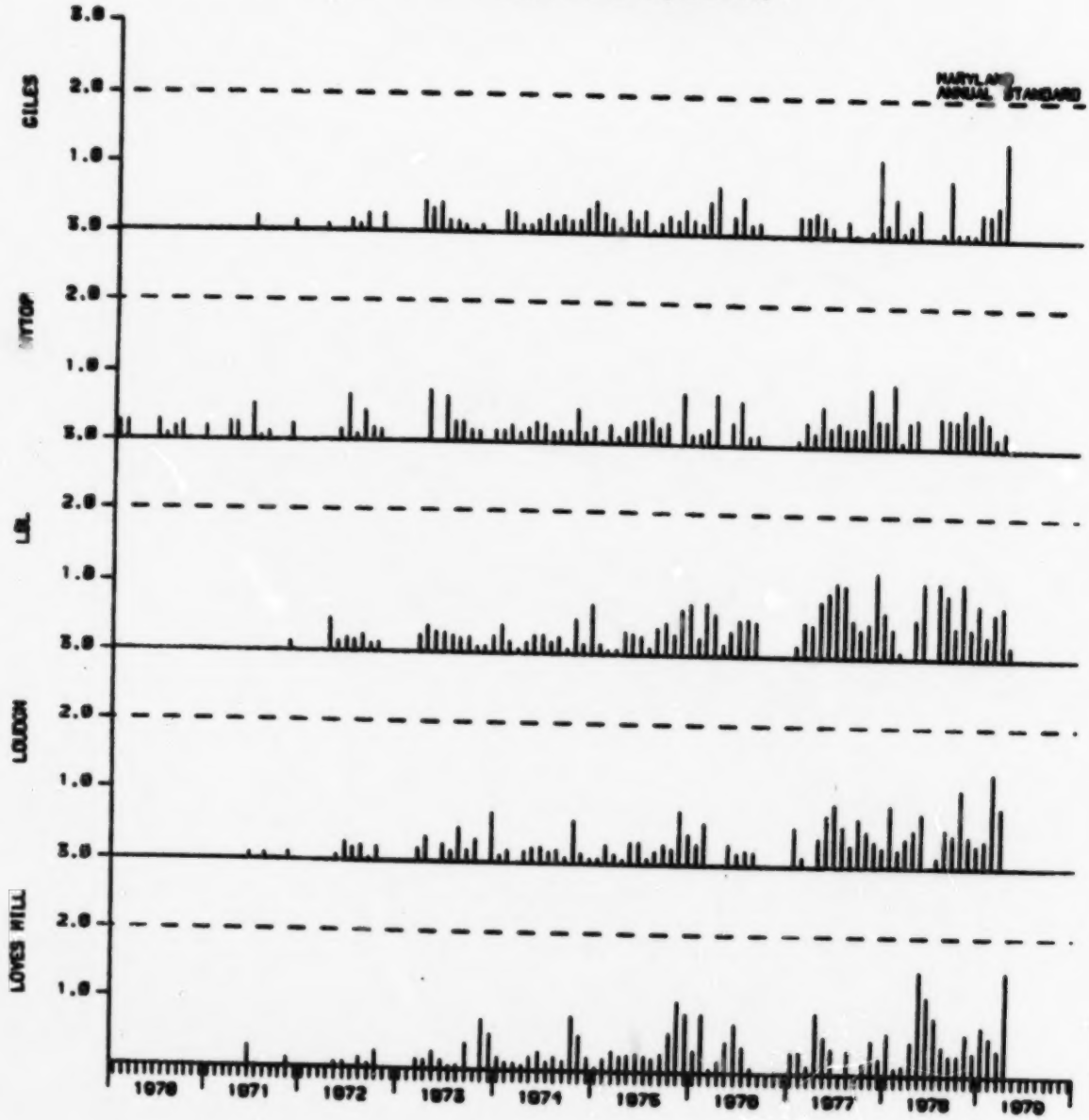
FIGURE 8 MONTHLY FLUORIDATION RATES AT THE TVA REGIONAL TREND STATIONS (1970-1979) (ug F/100 sq cm/day)



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